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High pressure solid–liquid equilibria of fatty acids

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Abstract

The solid–liquid phase diagrams of two binary mixtures of saturated fatty acids, formed by caprylic acid ($C_{8:0}$) + myristic acid ($C_{14:0}$) and lauric acid ($C_{12:0}$) + myristic acid ($C_{14:0}$), were measured using high pressure microscopy in the range of 0.1–90 MPa. It is shown that unlike for other long chain alkyl compounds such as alkanes the phase diagrams are only slightly affected by the pressure, even in very large pressure ranges such as studied in this work.

The modeling of the measured phase diagrams was attempted using an approach previously developed by the authors for *n*-alkane mixtures. It is here shown that this model can provide an accurate description of the high pressure solid–liquid equilibrium of fatty acid mixtures.

Keywords: Solid–liquid equilibrium; High pressure; Phase diagrams; Caprylic acid; Lauric acid; Myristic acid; Modeling

1. Introduction

Fatty acids are the major components of oils and fats [1]. They have critical implications in the understanding of the biological behavior of various lipid systems [2] and lately have been used in the production of coverings, plastics, and cleaning products [3], phase change materials for energy storage [4,5] and biodiesel. The knowledge about the properties of fatty acid mixtures can bring innovations in chemistry, food and pharmaceutical industries due to their influence on the characteristics of consumer products such as cosmetics and confectionary fats. The difficulties due the thermal decomposition in the isolation of fatty acids from their natural mixtures can be overcome through the adequate knowledge of their solid–liquid phase equilibrium.

The high pressure processing technique (HPP) is a non-heat technique used for food processing and food preservation [6]. This technique claims not to change the sensory and nutritious value of food maintaining the original freshness, color, flavor and taste of food [7,8]. It is however possible that the high pressure may cause changes in the crystal structure of the lipids and thus the raw material characteristics [8].

Some works with binary mixture of unsaturated fatty acids under high pressure have been presented before [9–11]. In these papers the authors emphasize the effect of pressure on polymorphic phenomena. Studies of the effect of high pressure on saturated fatty acid mixtures are not available in the literature.

Mixtures of saturated fatty acids exhibit in their phase diagrams invariant points, such as eutectic and peritectic points [12]. The presence of invariant points may have important consequences for choosing the criteria to be used in the separation or processing of fatty acid mixtures. This work investigates these behavior under pressure of two binary mixtures of saturated fatty acids that display the two different types of phase diagrams presented by saturated fatty acid mixtures: a pure eutectic phase diagram and a phase diagram presenting simultaneously eutectic and peritectic points. The fatty acid mixtures studied are caprylic acid ($C_{8:0}$) + myristic acid ($C_{14:0}$) and lauric acid

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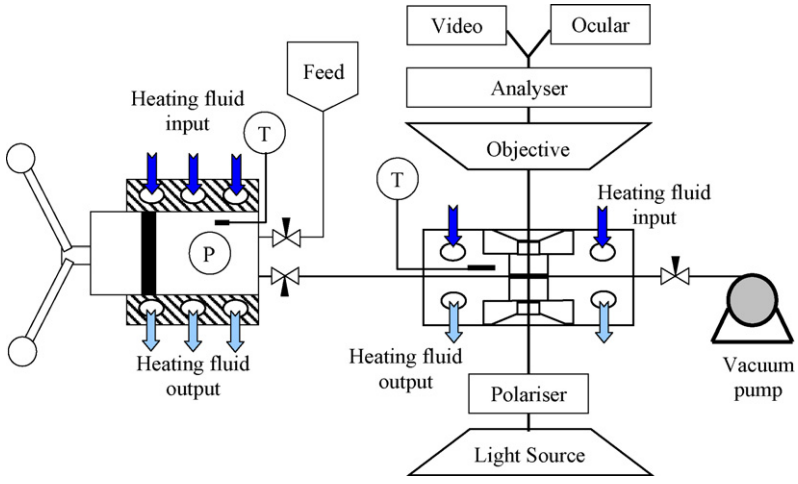

Fig. 1. High pressure microscopy apparatus.

($C_{12:0}$) + myristic acid ($C_{14:0}$) the liquidus curves of these systems were measured with a high pressure microscope [13,14] from atmospheric pressure up to 90 MPa. Data for these diagrams were previously measured at atmospheric pressure by Heintz (cited in Bailey [15] without mentioning to the method used) and recently [16,17] using a DSC technique. As mentioned before no data under pressure was available for saturated fatty acids.

2. Experimental section

Highly pure samples of caprylic acid (minimum 99%) supplied by Fluka and lauric acid and myristic acid (99–100%) supplied by Sigma were used in this work without further purification.

The mixtures were prepared using a high precision balance in order to achieve an accuracy of 0.02% in the molar fraction of the mixtures studied. Weighed quantities (5 g) of the binary mixture components were placed in a glass tube, where they were heated in an oven at a temperature of 350 K until fusion and homogenization of the mixture.

The high pressure solid–liquid equilibrium of the binary fatty acid mixtures was studied in a high pressure microscope developed previously [13,14]. This experimental apparatus is built around an autoclave cell, made up of a stainless steel block and equipped with two sapphire windows through which the studied sample can be observed with the help of a polarizing microscope coupled with a video camera. This technique allows the detection of very small crystals, down to 2 μm in size. A heat-transducing fluid that circulates in flow lines in the metallic thermostat block controls the temperature of the whole cell, which can be maintained between 243 and 373 K. The thermal regulation of this fluid is carried out by a thermostat bath (HUBER) with a temperature stability of 0.01 K. The sample temperature is measured by means of a platinum resistance thermometer (OMEGA) inserted inside a hole made in the cell. The uncertainty of temperature values is estimated at 0.2 K [13,14]. The pressure is transmitted to the sample through a hand pump and measured with a flush diaphragm pressure transmitter (DYNISCO), with a precision of 0.2%. This probe is regularly checked against a dead weight tester (BUDENBERG). The apparatus is sketched in Fig. 1.

The insertion of the sample into the microscope was achieved by maintaining the temperature of the pump and the cell around 333.15 K to avoid the crystallization of the sample. With the sample inside the cell the temperature was decreased 2–3 K below the melting temperature of the sample and kept at this temperature for 5–10 min. The temperature was then slowly increased until the beginning of the fusion and them the temperature was increased in steps of 0.1 K until the disappearance of the last crystal. After complete melting the pressure in the cell was increased resulting in the crystallization of the sample and a new temperature cycle was started.

3. Modeling

The modeling of the high pressure phase equilibria of fatty acids was carried using an approach previously proposed by us for alkane mixtures [18–23]. The model is here extended with success to fatty acids as follows.

Equilibrium conditions are obtained from the equality of fugacities of each component in the liquid and solid phase:

$$f_i^{\mathrm{L}}(T, P, x_i^{\mathrm{L}}) = f_i^{\mathrm{S}}(T, P, x_i^{\mathrm{S}}) \tag{1}$$

The liquid phase fugacities can be written as:

$$f_i^{\mathrm{L}}(T, P, x_i^{\mathrm{L}}) = P x_i^{\mathrm{L}} \phi_i^{\mathrm{L}} \tag{2}$$

where the fugacity coefficient ϕ_i^{L} is calculated using the Soave–Redlich–Kwong equation of state [24], with the LCVM mixing rules [25,26]. The volumetric properties calculated by the cubic EOS are corrected using the volume translation proposed by Peneloux et al. [27].

The solid phase fugacities at a pressure P are obtained by the equation:

$$\ln f_i^{\mathrm{S}}(P) = \ln f_i^{\mathrm{S}}(P_0) + \frac{1}{RT} \int_{P_0}^{P} \bar{V}_i^{\mathrm{S}} \, \mathrm{d}P \tag{3}$$

where the fugacity of the component i in the solid phase at pressure P_0 is calculated from its fugacity in subcooled liquid state